

LITHOGRAPHY METROLOGY PROGRAM

Advances in lithography have largely driven the spectacular productivity improvements of the integrated circuit industry, a steady quadrupling of active components per chip every three years over the past several decades. This continual scaling down of transistor dimensions has allowed more and more components on a chip, lowered the power consumption per transistor, and increased the speed of the circuitry. The shrinking of device dimensions has been accomplished by shortening the wavelength of the radiation used by the lithography exposure tools. The industry at this point has moved into the deep ultraviolet (DUV) spectrum. Currently, exposure tools operating at 193 nm are in leading edge manufacturing facilities. The first 193 nm immersion lithography tools will be shipped later this year. Development of exposure tools operating at 157 nm are “on hold” while high index fluids and lens materials for 193 nm tools are under intense exploration to develop high numerical aperture systems. If successful, the 157 nm tool generation may be bypassed. Looking beyond the deep ultraviolet, extreme ultraviolet radiation (EUV) at 13 nm is being investigated, and demonstration tools are being designed and assembled. The overall goal of this task is to support these developments in DUV and EUV. The areas of emphasis are characterization of lens materials, and immersion fluids, laser calorimetry, radiation detector sensitivity and damage, EUV lens metrology, and metrology for the development of advanced photoresist materials for both DUV and EUV.



METROLOGY SUPPORTING DEEP ULTRAVIOLET LITHOGRAPHY

GOALS

Develop solutions to key optical metrology issues confronting the semiconductor lithography industry. These include development of measurement methods and standards for characterizing deep ultraviolet (DUV) laser sources, detectors, and materials. One focus is on delivering high-accuracy measurements of DUV detector parameters and materials properties of immediate need by the industry. There is ongoing activity in the following areas: standards development, calibration services, characterization of optical materials, sources, and detectors, in addition to advising customers on in-house measurements.

CUSTOMER NEEDS

Increasing information technology requirements have created a strong demand for faster logic circuits and higher-density memory chips. This demand has led to the introduction of DUV laser-based lithographic tools for semiconductor manufacturing. These tools, which employ KrF (248 nm) and ArF (193 nm) excimer lasers, have led to an increased demand for accurate optical measurements at DUV laser wavelengths.

A new lithography technology, immersion lithography, depends on incorporating a high-index fluid between the optical system and the wafer and possibly also incorporating a high-index material as the last lens element. Design and development of 193 nm and 157 nm immersion lithographies require accurate measurements of the index properties of the potential 193 nm and 157 nm fluids and materials.

To support these efforts, the National Institute of Standards and Technology (NIST), with SEMATECH support, has developed a DUV metrology program focusing on the characterization of DUV optical materials, sources, and detectors.

The potential solutions for lithographic systems are discussed in the 2003 International Technology Roadmap for Semiconductors and its 2004 Update. On page 1 of the Update Lithography section, "...193 nm wavelength exposure systems, including 193 nm immersion systems... [may become] dominant solutions for the next two nodes... Furthermore, immersion lithography appears as potential solution at the 32 nm

and 22 nm nodes." The need for metrology in lithography is discussed on page 32 of the 2003 Metrology section on Integrated Metrology and Advanced Process Control, "Metrology plays a key role in productivity gains made through advanced process control (APC), particularly as the trend toward integrated metrology—from offline to inline to in situ techniques—enables a richer, more powerful spectrum of process control strategies."

TECHNICAL STRATEGY

■ High-accuracy measurements of the index properties of UV materials are required for the design of DUV lithography systems. NIST has been providing absolute index measurements at 193 nm and 157 nm with an accuracy of about 5 ppm to the industry using its DUV minimum-deviation-angle refractometer. To improve on this absolute accuracy, NIST has begun constructing a new state-of-the-art minimum-deviation system and separately developed another system based on a VUV FT spectrometer and a synchrotron radiation as a continuum source (see Fig. 1). Both of these systems will enable measurements to an accuracy of 1 ppm, and will be used to characterize high-index lens materials and immersion fluids for 193 nm and 157 nm lithography systems.

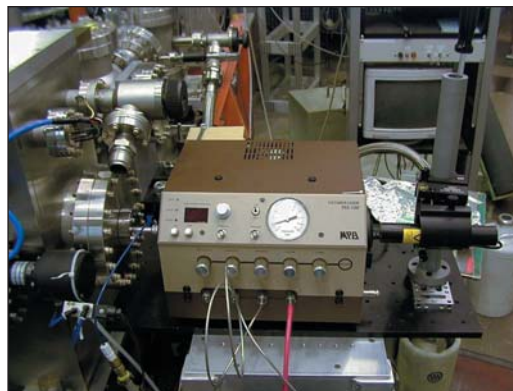


Figure 1. Facility for detector VUV radiation damage study using synchrotron radiation from SURF and a 157 nm excimer laser.

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"It's an excellent service NIST has performed for the entire industry. The kind of thing NIST is there for – to identify issues before the train wreck takes place."

Mordechai Rothschild, Massachusetts Institute of Technology's Lincoln Laboratory

DELIVERABLES: Index measurement capability with 1 ppm uncertainty. 3Q 2005

■ Taking full advantage of the potential resolution gain with immersion lithography may require using high-index materials as the last lens element, though as yet no such material has been demonstrated at 193 nm. To address this need we have begun, with the support of SEMATECH, a survey of candidate materials. We have identified several classes of oxide-based materials which have very high indices (near 2.0) at this wavelength and which can in principle be highly transparent at 193 nm. We have begun a program of complete optical characterization measurements of these materials to identify the most promising candidates and to assess their potential for development for lithography optics.

DELIVERABLES: Fully characterize the 193 nm optical properties of leading candidate high-index materials. 4Q 2005

■ An absolute light source in the DUV range based on synchrotron radiation using NIST's Synchrotron Ultraviolet Radiation Facility (SURF III) has been established using a dedicated beamline at SURF III. The flux of the DUV radiation at this beamline can be known to very high accuracy through the well established equations governing the behavior of the synchrotron radiation. The beamline is designed for customer calibration of a variety of DUV instruments to assist the development of the DUV lithography such as monochromators, discharge lamps, and irradiance meters. The spectral range covers all of the current important wavelengths for semiconductor industry such at 248 nm, 193 nm, 157 nm and even down to 13 nm. The uncertainty of such calibration is better than 1% in the case of deuterium lamp calibration.

DELIVERABLES: Provide customer DUV calibration for discharge lamps, monochromators, and irradiance meters using SURF III source-based beamline with highest accuracy. 4Q 2005

Beginning with the first edition of the National Technology Roadmap for Semiconductors (NTRS) in 1992, the semiconductor industry has made an organized, concentrated effort to reduce the feature sizes of integrated circuits. As a result, there has been a continual shift towards shorter exposure wavelengths in the optical lithography process. Because of their inherent characteristics, deep ultraviolet (DUV) lasers, specifically KrF (248 nm) and ArF (193 nm), and more recently F_2 (157 nm) excimer lasers, are the preferred sources for high-resolution lithography at this time. To meet the laser metrology needs

of the optical lithography community, we have developed primary standards and associated measurement systems at 193 nm and 248 nm, and 157 nm. Figure 2 shows the excimer laser calibration facility.



Figure 2. Laboratory for excimer laser energy and power meter calibrations, with measurement systems for 248 nm, 193 nm, and 157 nm. The excimer lasers are along the top right and the enclosures for nitrogen gas purging are in the foreground.

DELIVERABLES: Proved high-quality calibration services, and supporting measurements for excimer laser power and energy meters to the Semiconductor Industry at 248 nm, 193 nm, and 157 nm. Ongoing.

ACCOMPLISHMENTS

■ We have used our Hilger-Chance refractometer system to assist the industry in the search for appropriate high-index fluids (with n greater than water, 1.4366 at 193 nm) for possible use in immersion photolithography. In addition to providing measurement services to several companies which are developing new fluids for 157 nm and 193 nm lithography, we have performed our own survey of fluids at 193 nm. The results are shown in Fig. 3. As this figure shows, there are a number of fluids which are transparent at 193 nm and have n larger than water, up to 1.62 for glycerol. However, the thermo-optic coefficient, dn/dT , is larger as well, which may make their use in a commercial stepper system difficult because of thermal stability issues.

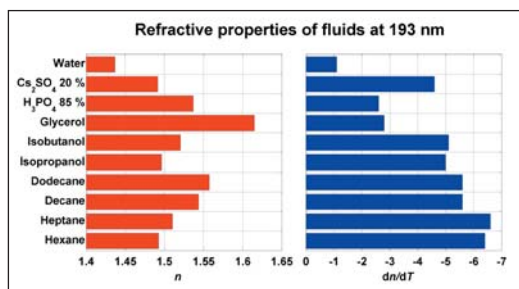


Figure 3. Measured index of refraction n and thermo-optic coefficient dn/dT of a number of potential immersion fluids for 193 nm lithography.

■ We have performed additional measurements of the effect of dissolved air on the refractive index of water at several wavelengths in the visible and UV and compared the results with predictions based on the equation of state of water and the known partial molar volumes and polarizabilities of the soluble components of air. The data and model calculations are in reasonable agreement, and demonstrate that the magnitude of the effect gets larger at shorter wavelength, up to -6.7×10^{-6} at 193 nm. While industry uses degassed water for immersion lithography, our results will enable any potential optical distortions due to air exposure to be modeled at the system level.

■ We have identified four major classes of oxide-based materials that have potential to be used as high-index lens materials for enabling further feature-size reduction with immersion lithography. The four classes are: 1) Group II oxides, *e.g.*, MgO, 2) crystalline spinel (MgAl_2O_4) and its variants, 3) a ceramic form of spinel, and 4) aluminum garnets, *e.g.*, YAG. We have made preliminary characterization measurements of the key 193 nm optical properties (see Fig. 4), including the intrinsic birefringence, of members of each of these classes needed to assess their suitability. As

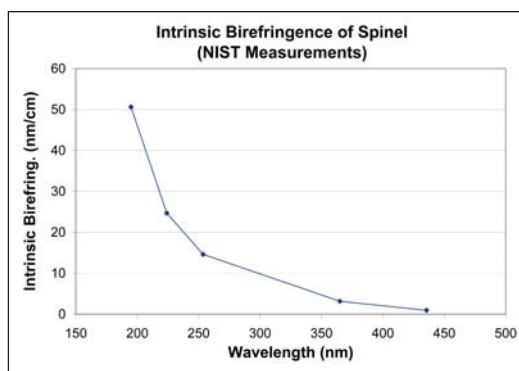


Figure 4. Measured intrinsic birefringence of crystalline spinel vs. wavelength.

a result of these measurements, several potentially feasible candidates have been established.

■ We have constructed a radiometric facility tailored for the DUV range using a beamline at NIST's SURF III with the radiation measurement scale derived from a high-accuracy cryogenic radiometer. The beamline is designed for very general-purpose high-accuracy measurements. We have used this facility to measure DUV general material properties such as transmission and reflectance. Examples of such measurements include DUV mirrors, windows, filters, and also the transmission and absorption of liquids that could be used for immersion lithography. On the detector side, we have calibrated and characterized a variety of DUV detectors such as solid state photodetectors, solar-blind detectors, photoconductive detectors, and pyroelectric detectors. We also performed irradiance calibrations for DUV irradiance meters.

■ We have built a facility at SURF III that allows simultaneous exposure of photodiodes to excimer radiation (see Fig. 5) and synchrotron radiation. Measurements of the spectral responsivity can be made in the spectral range from 130 nm to 320 nm with a standard uncertainty of less than 1 %. The intense, pulsed laser radiation was used to expose the photodiodes for varying amounts of accumulated irradiation whereas the low intensity, continuously-tunable cw radiation from the synchrotron source was used to characterize the photodiodes. The changes in the spectral responsivity of different kinds of diodes such as UV silicon, GaP, GaAsP, PtSi, diamond, and GaN were measured for a large range of total accumulated dose from an F_2 excimer laser operating at 157 nm. Differing amounts of changes were seen in different diodes depending on the total excimer irradiation dose and they showed different spectral changes in the responsivity as well. This yields important information about the mechanism responsible for the degradation of photodiodes. For example, we have determined that for silicon photodiodes under irradiation with a 157-nm excimer laser, an important mechanism for the degradation is the formation of trap states at the interface of the silicon-silicon dioxide induced by the damaging radiation. These trap states act as recombination centers and reduce the yield of electric current generated by incident radiation. A model was developed to simulate the change in response for photodiode irradiated by 157 nm radiation.



Figure 5. Measurement system for detector damage study by a 157 nm pulsed excimer laser.

■ During the last 15 years we have developed a suite of laser calorimeter standards for 248 nm, 193 nm, and 157 nm excimer laser energy and power measurements traceable to SI units. The 248 nm and 193 nm calorimeters use a specially designed absorbing cavity with a volume absorbing glass to reduce potential damage to the cavity by the high peak power in the UV laser pulses. The 157 nm calorimeter is a fundamentally new type of laser calorimeter standard that uses a thin-walled SiC absorbing cavity, which is designed to completely absorb and spread the incoming laser energy through multiple reflections. All of these calorimeters are calibrated using an imbedded electrical heater that allows for traceability to SI units through electrical standards of resistance and voltage. Calibrations for industry customers are accomplished for each wavelength with appropriate measurement systems that involve purging of oxygen to eliminate atmospheric absorption of the laser radiation.

■ As a further extension of our excimer laser services we have developed the capability to directly measure UV irradiance or “Dose” at 248 nm and 193 nm, which involves homogenizing the beam profile and measuring the energy transmitted through a calibrated aperture. This capability can improve accuracy for customers who need to measure the energy absorbed at a surface such as at the wafer plane.

■ We have also developed the capability to characterize the nonlinear response of 193 nm and 248 nm excimer laser detectors based on the correlation method. The method and system solves measurement difficulties associated with the temporal and spatial fluctuations of excimer laser pulse energy. Using this system, one can easily determine problems such as those due to the

incident pulse energy, range discontinuities associated with detector gain, and detector background noise (see Fig. 6).

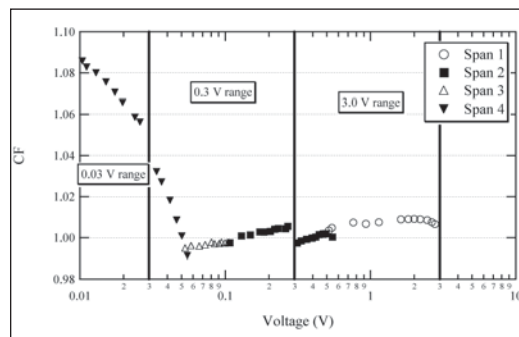


Figure 6. Nonlinearity measurement result of a 193 nm pulsed laser energy detector. CF is the correction for the detector's nonlinear response. The response is measured in four spans, covering 2.5 meter settings. The large degree of nonlinearity at the low end of the meter range is due to background effects.

■ We completed the first internal comparison of the NIST UV excimer laser calorimeters. This work includes measurements taken over the course of a two-year period in which the performance of the NIST 157, 193, and 248 nm excimer laser calorimeters was monitored at the design wavelengths as well as at the other excimer laser wavelengths. The results show good agreement among the transfer standards and excellent stability over time. From these data, we determined that the responsivity of the NIST UV laser calorimeters all agree within their stated uncertainties. In all but one case, the calorimeters' responsivities agree to better than 0.3 %. The comparison between the DUV (193 nm) and UV (248 nm) calorimeters at 248 nm uncovered a 1 percent difference between the calorimeters' responsivities. This difference is due to partial transmission of the 248 nm radiation through the absorbing glass of the DUV calorimeter which, reduces the calorimeter's absorbance and alters its response.

COLLABORATIONS

Air Products and Chemicals, Inc., Bridgette Budhlall, immersion photolithography fluid development.

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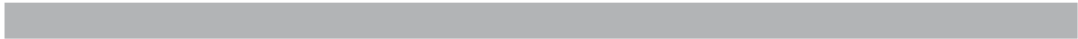
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METROLOGY SUPPORTING EXTREME ULTRAVIOLET LITHOGRAPHY

GOALS

Provide leading-edge metrology for the development and characterization of optical components and detectors used in Extreme Ultraviolet Lithography (EUVL). (EUVL utilizes radiation at 13.4 nm.)

CUSTOMER NEEDS

An intense international effort is presently underway to develop EUVL for the patterning of wafers beginning in about 2009. A milestone in the U.S. effort was the building of an alpha-tool called the ETS (Engineering Test Stand) that is housed at the Sandia National Laboratory. While the ETS has demonstrated the feasibility of EUVL for 70 nm design rules and beyond, much work needs to be done to improve the throughput, mask fabrication, and lifetime of the optics.

High resolution imaging with EUV radiation was not possible until the development of multilayer EUV mirrors in the mid 80s. This development has spawned the relatively new field of EUV optics and its associated set of new metrological challenges. Among these are: 1) precise EUV reflectivity maps; 2) EUV dosimetry; 3) EUV damage characterization; and 4) nanometer level optical figure measurement.

TECHNICAL STRATEGY

1. PRECISE EUV REFLECTIVITY MAPS

The present NIST/DARPA EUV Reflectometry Facility is located on a multipurpose beamline on the NIST Synchrotron Ultraviolet Radiation Facility (SURF III) storage ring. The beamline can provide a monochromatic beam of EUV or soft X-ray radiation in the 3 nm to 40 nm (400 eV to 30 eV) spectral range. Although primarily designed to serve the EUVL community by providing accurate measurements of multilayer mirror reflectivities, this beamline with its associated sample chamber has been used for many other types of measurements since the beamline's commissioning in early 1993. Among the other measurements performed recently are grating efficiencies, photocathode conversion efficiencies, phosphor conversion efficiencies, film dosimetry, and determination of EUV optical constants through angle dependent reflectance measure-

ments. A diagram of the NIST/DARPA EUV Reflectometry Facility is shown in Fig. 1.

Currently the NIST/DARPA facility is the only one in the U.S. large enough to measure optics larger than 200 mm in diameter. A recent international intercomparison among NIST and several other labs demonstrated reflectivity accuracy of 0.3 % and wavelength accuracy of 0.01 nm. Plans are under-way to reduce wave-length uncertainty by an order of magnitude.

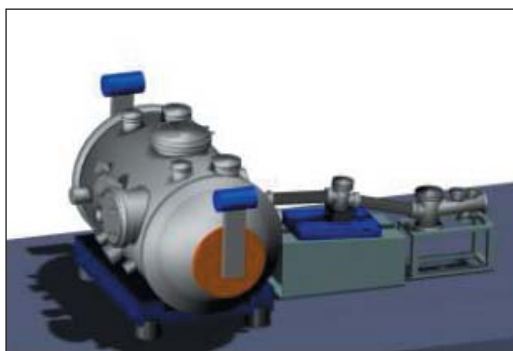


Figure 1. Diagram of NIST/DARPA EUV Reflectometry Facility, including the sample chamber and monochromator.

DELIVERABLES: Full reflectivity map of EUV mirrors up to 40 cm in diameter and 45 kg mass on an as needed basis for the EUVL community. Reflectivity and transmittance measurements of metrology components for EUVL community.

2. EUV DOSIMETRY

NIST is the primary national source for the radiometric calibration of detectors from the infrared to the soft X-ray regions of the spectrum. Until recently all NIST-characterized EUV photodetectors were calibrated on the SURF storage ring, which is essentially a cw source. Recently we have designed and built a pulsed EUV source similar to the source used in the ETS to calibrate EUV detectors for characterizing sources as well as wafer-plane dosimeters to be used in EUVL.

Two major concerns arise when using solid state photodiodes for detection of short pulse length radiation. First, while the average power may be quite modest, the peak power can be quite high. For example, a 10 Hz laser with an average power of 10 mW has a peak power of 100 kW for a 10 ns pulse. Photodiode saturation may

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seriously affect the linearity of EUVL dosimeters, even at fairly low average power levels. We have measured the limit of the linear operating range for an EUV sensitive Si photodiode using 532 nm radiation as a proxy for 13.4 nm; the absorption characteristics in Si are nearly identical. We have found that the photodiode responsivity is an inherently non-linear function of pulse energy, but the responsivity can be fit by a calibration function having two constant parameters. Use of the non-linear calibration function allows the photodiode to be used with reasonable uncertainty even when the responsivity has decreased due to saturation effects by as much as a factor of two. Defining the limit of linear operation as the pulse energy at which there is a loss of responsivity of 2 %, the total charge collected from a Si photodiode is a linear function of pulse energy at peak powers of 1 W (for an unbiased device) to 5 W (for a reverse bias of 10 V). The peak voltage developed is a linear function of pulse energy from 60 mW (unbiased) to 250 mW (10 V reverse bias). Currently, we are extending these results to determine the effect of the longer pulse lengths typical of EUVL plasma discharge sources, to understand the dependence on pulse energy density, and to explore a range of higher reverse bias conditions. A second concern is the equivalence of the responsivity under pulsed conditions and under the cw conditions of calibration facilities. We have compared the measured responsivity of a Si photodiode under pulsed conditions to the results of a low-power cw calibration. The low-power limit of the non-linear pulsed responsivity function is identical to the low-power cw responsivity with a relative standard uncertainty of 1 %. Thus, the results of a cw calibration may be transferred to a pulsed application if the pulse energy dependence is properly accounted for. Finally, we are investigating the saturation behavior using cw EUV radiation. The combination of these three conditions should lead to a good understanding of pulsed-EUV behavior.

We have developed a model of the physical processes that are responsible for the observed non-linear response function of the photodiodes. The loss of total collected charge is modeled as a result of recombination processes in the device during the electronic readout process. In this model, the decrease in the peak voltage developed arises from an increase in the junction capacitance due to the presence of the photogenerated electron-hole pairs, which act as a polarizable dielectric medium. The model correctly pre-

dicts the behavior of both calibration parameters as a function of reverse bias. To date, we have obtained results in the reverse bias range from 0 V to 10 V, and we will shortly be extending our observations to 150 V.

We have recently reduced the uncertainty of our cw radiometric scale in the neighborhood of 13 nm wavelength from the previous relative standard uncertainty of 4 % to 1 %. We accomplished this by operating an absolute cryogenic radiometer (ACR) on a high-throughput beamline at the SURF III synchrotron radiation facility and calibrating working standard photodiodes by direct comparison to the radiometer. The improved cw scale is transferred to the EUVL calibration facility described above to provide a U.S. national radiometric scale for detector-based pulse energy measurements at 13.5 nm wavelength with a relative standard uncertainty of a few percent.

Our group recently conducted the first ever responsivity measurements of an assembled Flying Circus metrology tool for EUVL on a pulsed EUV laser-produced plasma source, shown in Fig. 2.

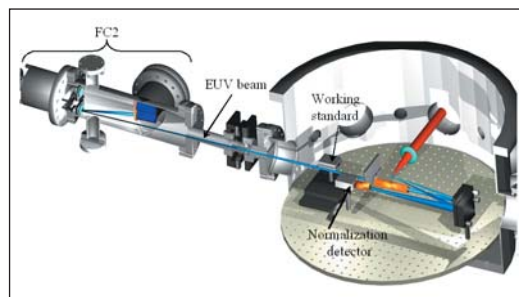


Figure 2. Flying Circus attached to laser-produced plasma source for calibration.

The Flying Circus (FC2) was developed by FOM (Foundation for Fundamental Research on Matter in the Netherlands). It is a filtered radiometer composed of Mo/Si Multilayer mirror, a thin film filter, and an EUV sensitive photodetector. The measurements were compared to the expected performance of the FC2 based on the NIST calibration of the FC2's individual components. The comparison found that there was a saturation effect in the NIST working standard detector, this was also predicted by the work noted above with visible light tests. The information and a model generated from those experiments was used to compensate for saturation effects in the working standard. With the saturation compensation, the resulting FC2 responsivity measurements were within 2 % to 3 % of that predicted by individual

component measurements. These measurements confirmed that EUV radiometry tools can incorporate calibrations based on individual component calibrations, thus eliminating the need for difficult assembled instrument calibrations. The experiments also allowed us to determine limits of linear performance for a commonly used EUV detector. Finally, our measurement and subsequent saturation modeling further substantiates the use of visible light as a proxy for EUV in detector saturation experiments.

In order to further our understanding of the saturation effects in silicon photodiodes we will continue to study the performance of these detectors under various pulse conditions. We will vary the spot size on these detectors to determine the effect of illumination area on saturation performance. In addition, we shall do a survey of several devices to determine the sample-to-sample dependence of saturation performance and develop tests that consumer's can use to determine the saturation onset levels of individual devices in house. Finally, we intend to expand our EUV measurement capabilities to include Synchrotron light-based measurements of EUV spectrograph and CCD responsivity to further aid the EUV lithography community.

DELIVERABLES: (1) EUV CCD responsivity Measurement Q3 2005 (2) EUV spectrograph measurement Q4 2005 (3) pulsed detector saturation evaluation Q3 2005

3. EUV DAMAGE CHARACTERIZATION

One of the potential showstoppers for commercialization of extreme ultraviolet lithography (EUVL) is the degradation of the multilayer-mirror stepper optics. The mirrors lose reflectivity because adsorbed contaminant gases such as hydrocarbons and water are cracked by the energetic (13.5 nm) photons. This leads to growth of an amorphous carbon layer on the optics surfaces or to oxidation of the optics themselves. The former effect is largely reversible; however, the latter is not. Unfortunately, these ambient contaminants cannot be eliminated by baking because the alignment of the mirror stack must be maintained to submicron tolerances. Various capping layers are currently being developed to extend the lifetime of the multilayer mirrors towards the required goal for commercialization of only a few per-cent reflectivity loss over 30 000 h of use.

To study the effectiveness of new capping layers and to better understand the underlying processes responsible for mirror degradation, NIST has commissioned a new beamline at the Synchrotron Ultraviolet Radiation Facility (SURF III) that can expose capped-multilayer samples to $\approx 6 \text{ mW/mm}^2$ of 13.5 nm radiation in an environment of controlled water or hydrocarbon partial pressures up to $6.7 \times 10^{-4} \text{ Pa}$. To date the most successful capping layer available to the community has been $\sim 2 \text{ nm}$ of ruthenium. Our exposure facility has demonstrated that multilayers with this capping layer suffer approximately one-tenth the reflectivity loss of bare Si-capped multilayers when exposed for $\approx 100 \text{ h}$ under rather aggressive conditions of $1 \times 10^{-4} \text{ Pa}$ of water vapor.

Clearly testing multiple capping layers for the required 30 000 h optic-lifetime is not feasible. So we are developing a program for accelerated lifetime testing which will expose multilayers to various intensities under various atmospheric conditions. The ultimate goal of this program is to develop a model of mirror damage that will enable the extrapolation of the years-long-lifetime under normal operating conditions from a few hundred hours of exposure under appropriately chosen accelerated exposure conditions. This effort requires an understanding of the underlying damage mechanisms that will be developed by an iterative series of controlled exposures and analysis. In addition to measuring the reflectivity loss of exposed multilayers, the damage will be characterized using a range of surface analysis techniques. Although this effort is just beginning, we have already discovered that small levels of hydrocarbons ($1 \times 10^{-7} \text{ Pa}$) can completely determine the rate of mirror damage, even in the presence of much larger partial pressures of water vapor ($7 \times 10^{-4} \text{ Pa}$). Thus the vacuum environment must be carefully controlled and well characterized for any accelerated testing procedure to produce meaningful results.

To respond to the growing need for optic-lifetime characterization we have continued to expand our capabilities. The original lifetime testing facility was developed with support from Sematech and Sandia National Labs. With intramural support from the Advanced Technologies Program this beamline will soon be expanded to deliver two orders of magnitude greater intensity. A second beamline is also being constructed with industry support to meet the testing throughput demands

of the larger EUVL community. In addition to expanding our facilities, we have also established very fruitful collaborations with experts in surface dynamics both within and outside the NIST community.

DELIVERABLES: (1) Carry out experiments on samples provided by EUVL community. (2) Work towards development of accelerated damage model by performing additional exposures and analyses; (3) Expand existing beamline to increase maximum exposure intensity a hundred fold; (4) Construct new lifetime testing beamline.

4. SUB-NM OPTICAL FIGURE MEASUREMENT

The commissioning of the “eXtremely accurate CALIBration InterferometerR” (XCALIBIR) at NIST is now complete and the instrument is fully functional (Fig. 3). The XCALIBIR interferometer is a multi-configuration precision phase-measuring interferometer for optical figure measurements of flat, spherical and aspheric optics that can achieve the very low measurement uncertainties that are required for the measurement of EUVL optics.

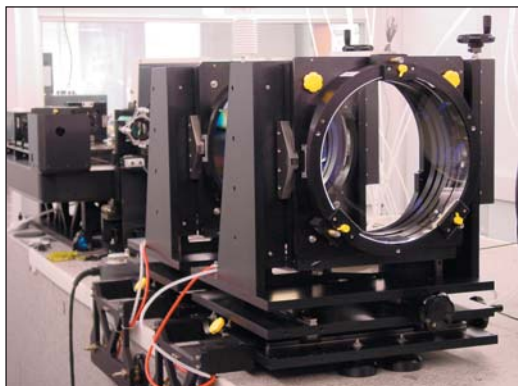


Figure 3. A view of the XCALIBIR interferometer.

The interferometer may be operated in either Twyman-Green or Fizeau configurations. A beam expander in the test arm of the interferometer provides a collimated test beam with 300 mm diameter. Transmission spheres are used to realize a spherical Fizeau interferometer for the testing of spherical and aspheric surfaces. The part under test is mounted on a remotely controlled 5+1-axis mount that can be moved on air bearings along a precision slideway in the direction of the optical axis of the interferometer. A system of three laser-interferometers tracks the movement of the test mount in the direction of the optical axis. A single-mode external cavity

diode laser (ECDL) is used as the light source in XCALIBIR. The laser frequency can be modulated to vary the effective temporal coherence over a wide range. Optical fibers with different core diameters are used to couple the light into the interferometer. The spatial coherence of the light source can thus be varied by changing the fiber core diameter.

The 300 mm diameter reference flats for the flat Fizeau configuration of the interferometer were calibrated with a 3-flat, 6-position self-calibration test. Figure 4 shows the topography of one of the reference flats. A large number of 3-flat measurements were made to estimate the measurement uncertainty. For each of the flats A, B, and C the *rms* of the difference between the averaged flat solutions and the individual measurements was plotted in a histogram (Fig. 5). A (statistical) measurement *rms* uncertainty of approximately 0.2 nm is evident.

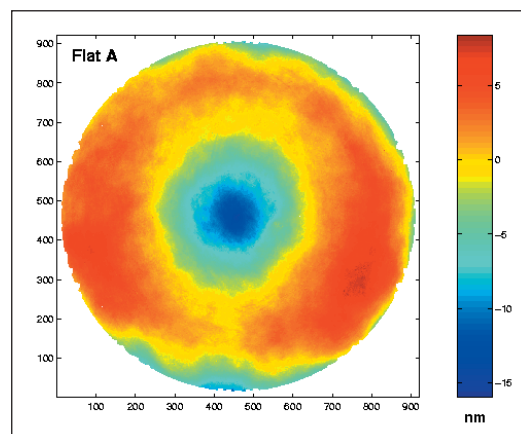


Figure 4. Topography of a 300 mm diameter XCALIBIR reference flat.

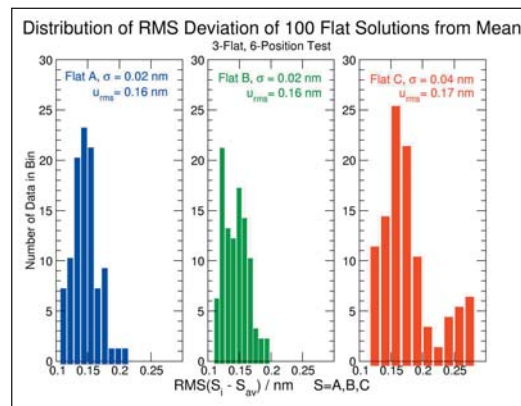


Figure 5. Distribution of rms deviations from best estimates surface (mean) for three flats A, B, and C.

When measurements of aspheric optics without null-optics are made, it is frequently the case that only a part, or subaperture, of a surface can be measured at once. For the figure measurement of the entire aspheric surface a number of overlapping subaperture measurements must then be combined, or “stitched” together. We have implemented flexible and robust algorithms for the stitching of subaperture measurements. To demonstrate the power of the stitching algorithm a precision silicon sphere was set up on a rotary table in XCALIBIR and the surface figure error was measured with an F/1.3 transmission sphere. 36 surface error measurements were made at 10° intervals. As shown in Fig. 6, the individual, overlapping, surface error measurements were then stitched together to form a map of the form error of the silicon sphere.

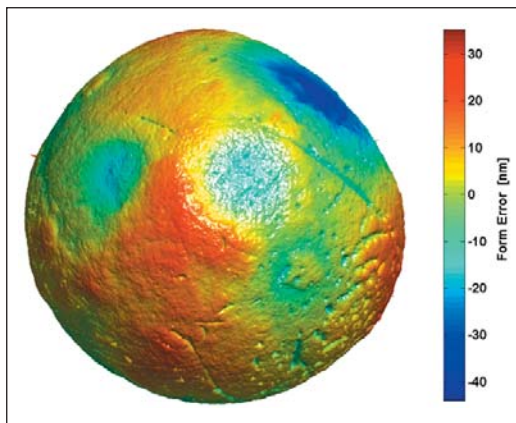


Figure 6. Topography of a precision silicon sphere, stitched from 132 measurements. The figure error is approximately 60 nm PV.

DELIVERABLES: Establish capability for measuring aspheric optics without null optics. 4Q 2003

ACCOMPLISHMENTS

■ IR² has undergone a major upgrade that enables us to address the metrology needs for 300 mm diameter wafers. A collimator lens has been installed that can illuminate the entire surface of a 300 mm wafer and thus allows us to make a measurement of the wafer’s thickness variation in a single measurement. The imaging system of the interferometer now can measure wafers with larger slopes and the spatial resolution of the detector was doubled. Further improvements will be aimed at reducing the noise level and at improving the measurement uncertainty.

■ The thickness variation (TTV) of a low-dopant double side polished silicon wafer has been characterized.

■ The flatness of 200 mm and 300 mm diameter wafers in the chucked condition was explored using the XCALIBIR interferometer.

COLLABORATIONS

VNL at Sandia National Laboratory, Leonard Klebanoff, Environmental team.

VNL at Lawrence Livermore National Laboratory, Saša Bajt, EUV Multilayer Development and Coating Team.

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POLYMER PHOTORESIST FUNDAMENTALS FOR NEXT-GENERATION LITHOGRAPHY

GOALS

In this project, we are developing an integrated program involving fundamental studies of photoresist materials to be correlated with resist performance metrics impacting next generation photolithography. We work closely with industrial collaborators to develop and apply high spatial resolution and chemically specific measurements to understand varying material properties and process kinetics at nanometer scales and to provide high quality data needed in advanced modeling programs. The understanding developed in this program will provide a detailed foundation for the rational design of materials and processing strategies for the fabrication of sub 50 nm structures. The unique measurement methods we apply include X-ray and neutron reflectivity (XR, NR), small angle neutron scattering (SANS), near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, quartz crystal microbalance (QCM), nuclear magnetic resonance (NMR), atomic force microscopy (AFM), fluorescence correlation spectroscopy (FCS) and combinatorial methods. Our efforts focus on the fundamentals of polymeric materials and processes that control the resolution of the photolithography process including: (1) the physical properties of and polymer chain conformation within sub 50 nm structures; (2) the spatial segregation and distribution of photoresist components; (3) the transport and kinetics of photoresist components, and the deprotection reaction interface over nanometer distances; (4) the material sources of line-edge roughness (LER), a measure of the ultimate resolution of the lithographic process; (5) the polymer physics of the developer solution and the dissolution process; and (6) influence of moisture on the thermophysical properties of interfaces as applicable to immersion lithography. These data are needed to meet the future lithographic requirements of sub 50 nm imaging layers and critical dimensions.

CUSTOMER NEEDS

Photolithography remains the driving and enabling technology in the semiconductor industry to fabricate integrated circuits with ever decreasing feature sizes. Today, current fabrication facilities use chemically-amplified (CA) photoresists, complex and highly tuned formulations

of a polymer film loaded with photoacid generators (PAGs) and other additives. Upon exposure of the photoresist film through a mask, the PAG creates acidic protons. A post-exposure bake is then applied and the acid protons diffuse and catalyze a deprotection reaction on the polymer that alters its solubility in an aqueous base developer solution. These reaction, diffusion, and development processes must be understood and controlled at the nanometer length scale to fabricate effectively integrated circuits. Chemically amplified resists are also deposited onto bottom anti-reflection coatings (BARCs). Interactions and component transport between the BARC and resist layer can lead to loss of profile control or pattern collapse. Detailed studies of these interaction and transport mechanisms are needed to design materials for the successful fabrication of sub 50 nm structures.

There are significant challenges in extending this technology to fabricate the smaller feature sizes (sub 50 nm) needed to continue performance increases in integrated circuits. First, new radiation sources with shorter wavelengths (193 nm, 157 nm, or EUV) require photoresist films nearing 100 nm thick to ensure optical transparency and uniform illumination. In these ultrathin films, confinement can induce deviations in several key materials parameters such as the macromolecular chain conformation, glass transition temperature, viscosity, or transport properties. Furthermore, the required resolution for a sub 50 nm feature will be on the order of 2 nm, approaching the macromolecular dimensions of the photoresist polymers. It is not yet clear how deviations due to confinement will affect the ultimate resolution in these ultra-thin photoresist films. Additionally, the material sources of feature resolution (line-edge and sidewall roughness) and profile control need to be identified and understood to ensure the success of needed patterning technologies.

The requirements for advanced photoresists are discussed in the 2004 International Technology Roadmaps for Semiconductors on page 3, Lithography Section, "Photoresists need to be developed that provide good pattern fidelity, good linewidth control (including roughness), and low defects. As feature sizes get smaller, defects and

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"[This work] opens a window of opportunity to construct structure-property relationships between chemical transport mechanisms and ultimate resist resolution. It may also lead to insights into the ultimate, intrinsic resolution limits and critical dimension control of polymer-based imaging materials."

*E. Reichmanis and
O. Nalamasu, Bell Labs, Lucent
Technologies, Science, 297,
349 (2002).*

polymers will have comparable dimensions with implications for the filtering of resists.”

TECHNICAL STRATEGY

In this project, we use model photoresist materials to validate the new measurement methods. Model photoresist materials (248 nm, 193 nm, 157 nm, and EUV) have been used initially to address several important fundamental questions including the thermal properties of ultrathin films as a function of film thickness and substrate type, the conformation of polymer chains confined in ultrathin films, the surface concentration of PAGs, the diffusion and the reaction kinetics of the deprotection reaction, and the physics of the development process. We also are adapting the application of combinatorial methods as a tool to determine rapidly important lithographic parameters and to identify material factors impacting feature resolution. These results provide a strong basis for understanding the material property changes that may affect the development of lithography for sub-50 nm structures using thin photoresist imaging layers. The interaction between model photoresists and BARC materials also requires detailed experimental investigation to optimize the materials factors impacting lithographic performance.

DELIVERABLES: Develop model thin films to measure the transport and kinetics of photoresist components and the deprotection reaction as a function of PAG size and resist copolymer chemistry. 2Q 2005

DELIVERABLES: Conclude protection degree effect on the dissolution and swelling behavior and the relationship to surface roughness for 193 nm photoresist polymers. 3Q 2005

DELIVERABLES: Utilize reaction-front bilayer geometry to identify and quantify the effects of developer solution parameters (base concentration, ionic strength) on the final resolution of lithographic materials. 3Q 2005

DELIVERABLES: Quantify surface segregation, surface deprotection chemistry, distribution of photoresist components (resist, photoacid, base additive) in 193 nm resists, using NEXAFS. 4Q 2005

DELIVERABLES: Develop immersion metrology methods using NR and QCM to quantify developer profiles within ultrathin photoresist films. 2Q 2005

ACCOMPLISHMENTS

■ The molecular origin of dimensional changes within ultrathin films when exposed to developer

solutions was measured using neutron reflectivity. A model 157 nm photoresist material provided needed in the fundamentals of material sources to line-edge roughness. Quartz crystal microbalance measurements complement these measurements with the added ability to measure the kinetics of swelling, however, the profile and chemical specificity are exclusively obtained with NR.

These new measurement methods, applicable to immersion lithography, demonstrate that swelling and aqueous base penetration must be considered to improve dissolution models involving solid-liquid interfaces. The aqueous base profile, shown in Fig. 1, illustrates the penetration of the small base molecule throughout the thin film as a function of developer strength. The swelling, due to polyelectrolyte effects, was predicted in FY03. The influence of moisture and interfacial energy are also probed using NR, XR, and quartz crystal microbalance techniques allowing a complete equilibrium and kinetics measurement methods.

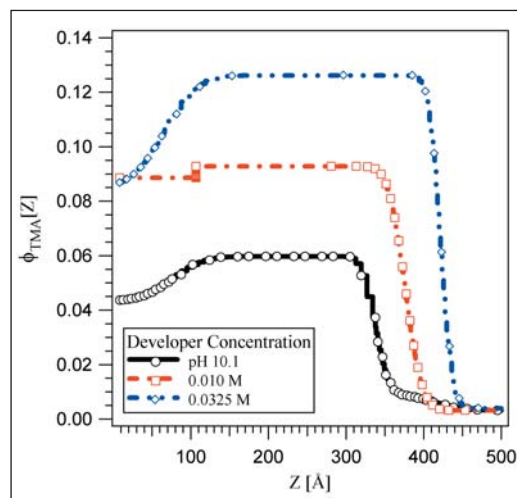


Figure 1. Developer Fundamentals for LER. Direct measure of the base concentration dependence of swelling and deuterated tetramethyl ammonium ion profile throughout the thickness, of a model 157 nm photoresist using liquid immersion neutron reflectivity.

■ After photogeneration, acid molecules catalyze multiple reactions within the photoresist matrix. A central issue in photoresist design is quantifying both the number of reactions each acid can catalyze and the size and shape of the deprotected volume created upon reaction. The size and shape of the volume have been identified in recent computer simulations as a primary source line edge roughness (LER) formation.

Using SANS and specially deuterated polymers, we successfully measured characteristics of the deprotection volume due to acid diffusion paths in a model photoresist. The general technique is readily extendible to photoresists with the appropriate deuterium labeling, independent of the PAG species. The deprotection volume from dispersed acid molecules features a diffuse interface, a result inconsistent with a well-defined two-phase structure. The data in Fig. 2 are consistent with models for random walk statistics. We determined that the deprotection volume has a radius of approximately 8.5 nm after 120 s of post exposure bake at 90 °C. Infrared spectroscopy was used to determine the level of deprotection at 32 % with a 0.7 % mass fraction of PFOS. The result is consistent with a large diffusion path, and hence a large number of catalyzed reactions per acid molecule.

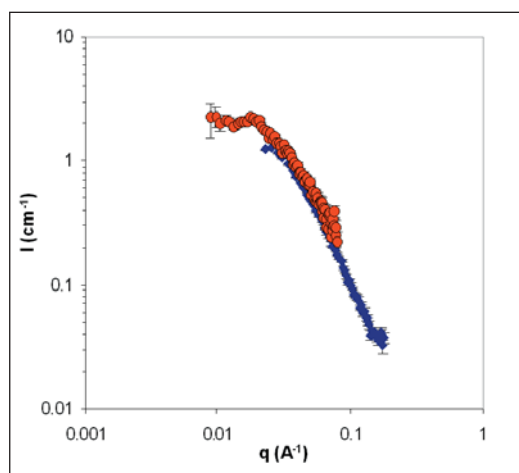


Figure 2. SANS data from the deprotection of dispersed PAGs after exposure and bake. The data are consistent with a random walk deprotection reaction path.

■ The deprotection reaction front profile was measured with nanometer resolution by combining neutron reflectivity and FTIR on a bilayer structure prepared with model 193 nm photoresists. The upper layer of the structure is loaded with the photoacid generator. Upon exposure and baking, the acid diffuses into the lower layer and catalyzes the deprotection reaction. The protecting group partially leaves the film, quantified by FTIR, upon reaction. The contrast to neutrons results from the reaction allowing for observation of the reaction front. By comparing the reaction front to the developed film profile, we obtain important insight into both the spatial extent of

the reaction and the development process itself. These data are the first available with this spatial resolution and are critically needed for the development of process control over nanometer length scales. We find that the reaction front broadens with time while the surface roughness of the developed structure remains relatively sharp. Additionally, we find that the reaction front width is dependent upon resist chemistry and PAG size. These experimental data provides a rational design of next-generation photoresist component from the resist chemistry to the reaction-diffusion process.

■ NEXAFS measurements were used to measure the surface concentration of photoresist and BARC components and the surface reaction kinetics in model photoresist polymers as a function of common processing conditions. A significant advantage of the NEXAFS measurement is the capability of separating interfacial and bulk signals within the same sample and experiment in Fig. 3. NEXAFS measurements of interfacial chemistry are possible because of the limited escape depth of produced secondary electrons. By separately observing the electron and fluorescence yield, the chemistry at the surface (2 nm) and bulk (200 nm) may be determined. Different chemistries may be observed by examining the near-edge x-ray spectra of light elements such as carbon, oxygen, fluorine, and nitrogen. In this way, changes in the surface chemistry relative to the bulk film can be investigated as a function of lithographic processing steps such as exposure and heating. We have found that fluorinated PAG molecules preferentially segregate to the film surface. The relative amount of segregation is dependent upon the specific polymer chemistry and PAG size. In addition, NEXAFS analysis of residual layers arising from BARC-resist component transport

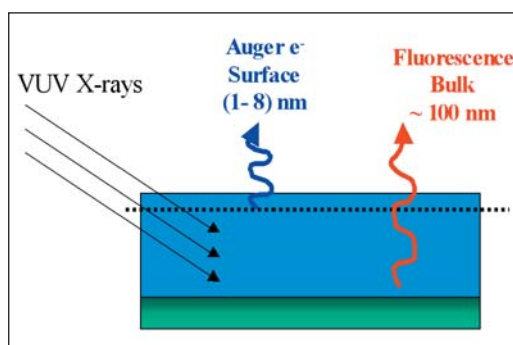


Figure 3. Schematic diagram of the NEXAFS measurement geometry. Spectra are obtained from the film surface and bulk simultaneously.

and interactions enable detailed analysis of potential mechanisms leading to loss of profile control. UV exposure, post-exposure bake, and a novel atmosphere controlled chamber have been developed to test environmental stability against model airborne contaminants and influence on *in situ* processing.

■ The development step selectively removes UV exposed photoresist material and represents the last step in the fabrication of nanostructures prior to semiconductor etch and deposition. With dimensions shrinking to sub-50 nm, control of line-edge roughness becomes more important and contributions to roughness from the development step requires an improved framework. In the development step, the aqueous base TMAH developer shifts the local chemical equilibrium from an unionized form to the ionized form, for instance in the 248 nm material poly(hydro-xy-styrene). SANS data, in Fig. 4, demonstrate the origin of the miscibility in aqueous base is due to the ionization of the photoresist leading to polyelectrolyte behavior. The identification of the presence of polyelectrolyte behavior during the development process provides an improved framework to understand the roles of added electrolytes, such as low molecular weight organic (tetramethylammonium chloride) and inorganic salts (NaCl, KCl). The addition of salts reducing the influence of polyelectrolyte behavior. Current experiments with different developing and rinsing protocols demonstrate that the pH of the rinse step is very important. This suggests the surface layer may contain polyelectrolyte effects even after development as demonstrated by an increase in

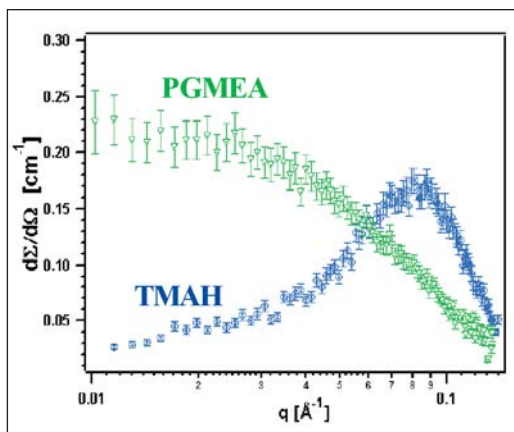


Figure 4. SANS data from a model photoresist polymer in organic solvent (PGMEA) and the developer base solution (TMAH). The scattering peak in TMAH solution is representative of the polyelectrolyte behavior.

surface RMS roughness for the development of bilayer samples with 0.26N TMAH followed by water rinse and 0.01 M HCl rinse.

■ Characterization of local bulk scale mixing is necessary for understanding future photoresist materials as feature dimensions are reduced to sub-65 nm. The intimacy of mixing of PAG and photoresist was probed by solid state proton NMR methods based on inversion-recovery, solid-echo-spin-diffusion, and chemical-shift-based-spin-diffusion pulse sequences. The effect of PAG concentration on the dispersion and phase separation within bulk blends was found to depend strongly on the photoresist chemistry (see Fig. 5). In model 248 nm materials PFOS was found to mix on the molecular scale for loadings between 9 and 45 %; hence the two components are thermodynamically miscible in this range. These results were extended to a challenging 157 nm formulation and revealed that while PFOS is miscible within the two photoresists – the ternary system exhibit phase separation into domains exceeding 30 nm.

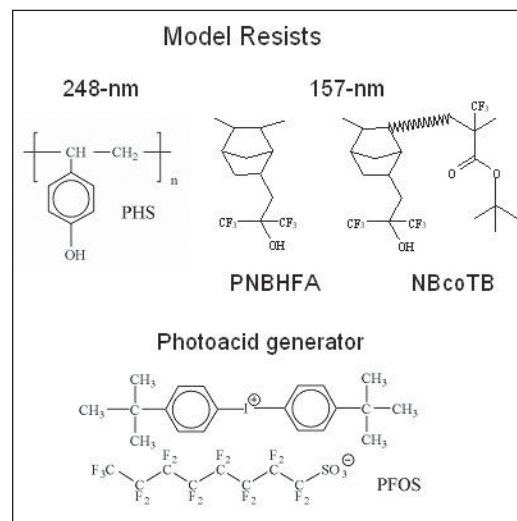


Figure 5. Model 248 nm and 157 nm photoresist materials used to probe the intimacy of mixing of photoacid generator in blends by NMR methods.

COLLABORATIONS

Polymers Division, NIST – Bryan D. Vogt, Shuhui Kang, Ashwin Rao, David VanderHart

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DuPont Electronic Polymers L.P. – Jim Sounik, Michael T. Sheehan

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Intel – CRADA 1893

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